A

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
REQUEST FOR FILING NATIONAL PATENT APPLICATION

Under 35 USC 111(a) and Rule 53(b)
(Not for Provisional or PCT cases)
WITH SIGNED DECLARATION

PATENT APPLICATION

jc658 U.S. PTO
05/17/99

jc551 U.S. PTO
09/312811
05/17/99

Asst. Commissioner of Patents
Washington, D.C. 20231

NONPROVISIONAL
NON REISSUE

Sir:

Herewith is the PATENT APPLICATION of
Inventor(s): GIARDELLO et al.

(Our Deposit Account No. 03-3975)

	C#	M#
Our Order No.	14518	0261607

Title POLYOLEFIN COMPOSITIONS OPTIONALLY HAVING VARIABLE TOUGHNESS AND/OR HARDNESS

	M#	Client Ref
Atty. Dkt.:	PM 0261607	ASM-110

including:

Date: 05/17/99

1. Specification: 30 pages (only spec. and claims)
2. ☐ Specification in non-English language
3. Declaration ☒ Original ☐ Facsimile/Copy ☐ Abstract 1 page(s); 24 numbered claims

3(a). ☐ Drawings: _______ sheet(s) ☐ informal; ☐ formal of size: ☐ A4 ☐ 11"

4. ☒ See top first page re prior Provisional, National or International application(s). ("X" box only if info is there and do not complete corresponding item 5 or 6). (Prior M# 253449 SN 60/085,981)
5. **AMEND the specification** please by inserting before the first line: -- This is a ☐ Continuation-in-Part ☐ Divisional ☐ Continuation ☐ Substitute Application (MPEP 201.09) of:

5(a). ☐ National Appln. No. ____/________ filed ______. (M# ____)

5(b). ☐ International Appln. No. __________ filed __________ which designated the U.S.

6. ☐ **AMEND the specification** by inserting before the first line: -- This application claims the benefit of U.S. Provisional Application No. 60/________, filed __________. --
7. ☐ Attached is an assignment and cover sheet. Please return the recorded assignment to the undersigned.
8. ☐ Prior application is assigned to
   by Assignment recorded __________ Reel __________ Frame __________
9. **FOREIGN** priority is claimed under 35 USC 119(a)-(d)/365(b) based on filing in __________

Application No.	Filing Date	Application No.	Filing Date
(1)		(2)	
(3)		(4)	
(5)		(6)	
(7)		(8)	
(9)		(10)	

10. _______ (No.) Certified copy (copies): ☐ attached; ☐ previously filed (date) __________
   in U.S. Application No. ____/________ filed on __________
11. ☒ Attached: 1 (No.) Verified Statement(s) establishing "small entity" status under Rules 9 & 27.
12. **DOMESTIC/INTERNATIONAL** priority is claimed under 35 USC 119(e)/120/365(c) based on the following provisional, nonprovisional and/or PCT international application(s):

Application No.	Filing Date	Application No.	Filing Date
(1) 60/085,981	05/19/98	(2) 60/118,865	02/05/99
(3)		(4)	
(5)		(6)	
(7)		(8)	
(9)		(10)	

13. ☐ Attached:

14. ☒ This application is being filed under Rule 53(b)(2) since an inventor is named in the enclosed Declaration who was not named in the prior application.

15. ☐ Preliminary Amendment:

THE FOLLOWING FILING FEE IS BASED ON CLAIMS AS FILED LESS ANY ABOVE CANCELLED

				Large/Small Entity		Fee Code
16. Basic Filing Fee				$760/$380	$380	101/201
17. Total Effective Claims	24	minus 20 =	*4	x $18/$9 =	+ 36	103/203
18. Independent Claims	2	minus 3 =	*0	x $78/$39 =	+ 0	102/202
*If answer is zero or less, enter "0"						
19. If any proper multiple dependent claim (ignore improper) is present, add (Leave this line blank if this is a reissue application)				+ $260/$130	+ 0	104/204
20. TOTAL FILING FEE ENCLOSED =					$416	
21. If "non-English" box 2 is X'd, add Rule 17(k) processing fee				+ $130	+ 0	139
22. If "assignment" box 6 is X'd, add recording fee				+ $40	+ 40	581
23. ☐ Attached is a Petition/Fee under Rule No.				+ $130	+ 0	122
24. TOTAL FEE ENCLOSED =					$456	

CHARGE STATEMENT: The Commissioner is hereby authorized to charge any fee specifically authorized hereafter, or any missing or insufficient fee(s) filed, or asserted to be filed, or which should have been filed herewith or concerning any paper filed hereafter, and which may be required under Rules 16-18 (missing or insufficient fee only) now or hereafter relative to this application and the resulting Official document under Rule 20, or credit any overpayment, to our Account/Order Nos. shown in the heading hereof for which purpose a duplicate copy of this sheet is attached.

This CHARGE STATEMENT does not authorize charge of the issue fee until/unless an issue fee transmittal form is filed.

Pillsbury Madison & Sutro LLP
Intellectual Property Group

1100 New York Avenue, N.W.
Ninth Floor, East Tower
Washington, D.C. 20005-3918
Tel: (202) 861-3000
JYB/jlv

By Atty: **John E. Burke** **Reg. No.** **35836**

Sig: [signature]

Fax: (202) 822-0944
Tel: (202) 861-3000

NOTE: **File in duplicate with 2 post card receipts (PAT-103) & attachments**

Inventor(s): GIARDELLO et al. (Atty. Dkt.
Appln. No.: / or Patent No.: 261607/ASM-110
Filed: 05/17/99 or Issued.: M# / Client Ref.
Title: POLYOLEFIN COMPOSITIONS OPTIONALLY HAVING VARIABLE TOUGHNESS AND/OR HARDNESS

SMALL ENTITY STATEMENT CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(d) and 1.27 (c)) - **SMALL BUSINESS CONCERN**

I hereby state that I am

☐ the owner of the small business concern identified below:
☒ an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN MATERIA, INC.
ADDRESS OF CONCERN 2531 NINA STREET, PASADENA, CALIFORNIA 91107

I hereby state that the above identified small business concern qualifies as a small business concern as defined in 13 CFR 121.12, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under Section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby state that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention **entitled:** POLYOLEFIN COMPOSITIONS OPTIONALLY HAVING VARIABLE TOUGHNESS AND/OR HARDNESS
by inventor(s) GIARDELLO et al. described in

x → ☒ the specification filed herewith,
one → ☐ Application No. 0 / , filed
box → ☐ Patent No. , issued

If the rights held by the above identified small business concern are not exclusive, each small entity individual, concern or organization having rights to the invention is listed in (A) and (B) below and no rights to the invention are held by any person, other than the inventor, who could not qualify under 37 CFR 1.9(c) as an independent inventor if that person had made the invention, or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

(A) FULL NAME of assignee/licensee/grantee/conveyee*
ADDRESS
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

(B) FULL NAME of assignee/licensee/grantee/conveyee*
ADDRESS
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

*NOTE: Separate statement is required from each person, concern or organization named in (A) and (B) above having rights to the invention, averring to his/her/its status as a small entity. (37 CFR 1.27)

I acknowledge the duty to file, in this case, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

NAME OF PERSON SIGNING MICHAEL A. GIARDELLO
TITLE OF PERSON OTHER THAN OWNER CHIEF EXECUTIVE OFFICER
ADDRESS OF PERSON SIGNING 2531 NINA STREET, PASADENA, CALIFORNIA 91107

SIGNATURE [signature] DATE 5/14/99

APPLICATION UNDER UNITED STATES PATENT LAWS

Invention: POLYOLEFIN COMPOSITIONS OPTIONALLY HAVING VARIABLE TOUGHNESS AND/OR HARDNESS

Inventor(s): MICHAEL A. GIARDELLO
JONATHAN G. LASCH
CHRISTOPHER J. CRUCE
JESSIE G. MACLEOD

Pillsbury Madison & Sutro LLP
Intellectual Property Group
1100 New York Avenue, N.W.
Ninth Floor, East Tower
Washington, D.C. 20005-3918
Attorneys
Telephone: (202) 861-3000

This is a:

- ☐ Provisional Application
- ☒ Regular Utility Application
- ☐ Continuing Application
- ☐ PCT National Phase Application
- ☐ Design Application
- ☐ Reissue Application
- ☐ Plant Application
- ☐ Substitute Specification
  Sub. Spec. filed ______
  in App. No. _____/_____
- ☐ Marked Up Specification re
  Sub. Spec. filed ______
  in App. No. _____/_____

SPECIFICATION

POLYOLEFIN COMPOSITIONS HAVING VARIABLE TOUGHNESS AND/OR HARDNESS

This application claims the benefit of co-pending U.S. Provisional Patent Application Serial Nos. 60/085,981, filed May 19, 1998; and 60/118,865, filed February 5, 1999.

FIELD OF THE INVENTION

The present invention is directed generally to novel polyolefin compositions having variable toughness and/or hardness properties, and to articles of manufacture produced therefrom. More specifically, the present invention relates to dicyclopentadiene-based polymers (poly-DCPD) comprising various toughness and/or hardness modulators.

BACKGROUND OF THE INVENTION

During the past twenty-five years, research efforts have enabled the elucidation of olefin metathesis reactions catalyzed by transition metal complexes. In particular, certain ruthenium and osmium carbene compounds have been identified as effective catalysts for olefin metathesis reactions such as, for example, ring opening metathesis polymerization (ROMP). Such metathesis catalysts have been previously described in, for example, United States Patent Nos. 5,312,940; 5,342,909; 5,728,917; 5,710,298; and 5,831,108; PCT Publications WO 97/20865 and WO 97/29135; and in United States Provisional Patent Application No. 60/115,358, filed January 8, 1999 by inventors Steven P. Nolan and Jinkun Huang entitled "Novel Metathesis Catalyst Compositions and Methods for Their Use," the disclosures of which are incorporated herein by reference.

Examples of olefin monomers that may be polymerized using the aforementioned metathesis catalysts include dicyclopentadiene (DCPD), in addition to other strained cyclic olefin compounds. Polymer compositions, and articles or parts produced therefrom, are useful in a wide variety of applications because of their unique physical properties and ease of fabrication. In particular, poly-DCPD compositions show promise for applications requiring a combination of toughness, hardness, elasticity, rebounding qualities, marine anti-fouling and/or corrosion

resistance, among other properties. In addition, the low viscosity of DCPD-based compositions makes these resins particularly well-suited to the fabrication of complex shapes and composites.

Numerous common polymer additives, including pigments, dyes, plasticizers, rubber particles and antioxidants, among others, have been included in polymer compositions in an effort to vary or preserve over time one or more physical properties of the polymer. However, these additives may also effect unintended or undesirable changes in one or more physical properties. Thus, it has not been possible using traditional high-viscosity thermoset resins to vary the hardness, toughness or surface "feel" of the resin compositions, or parts thereof, through the addition of these additives without compromising one or more desirable properties of the native polymer. In addition, the surface "feel" or texture, as well as the elasticity, toughness and hardness of a polymer composition, or parts made thereof, may be important considerations in certain commercial applications.

In light of the foregoing, there exists a need for polymer compositions, and articles of manufacture thereof, which may be formulated to have variable toughness and/or hardness for use in a wide range of commercial applications. This is especially so for materials related to the sports, recreational and marine industries. Preferably, the compositions' properties are not compromised by the incorporation of additives giving rise to the beneficial toughness and/or hardness characteristics.

SUMMARY OF THE INVENTION

The present invention relates to novel polyolefin compositions having variable toughness and/or hardness properties, to methods of making the compositions, and to articles of manufacture produced therefrom. In particular, the present invention provides for toughness/hardness modulating additives, which may be added to polyolefin resins. These toughness/hardness modulators permit controllable modulation of the surface "feel", toughness and/or hardness of a polyolefin article or part. Such modified polyolefin compositions are useful in a variety of applications and products, particularly those in the sports, recreational, and marine fields.

In certain preferred embodiments, the polyolefin compositions of the present invention are prepared by the ring-opening metathesis polymerization (ROMP) of

dicyclopentadiene (DCPD) and related strained cyclic olefins, polymerized with a metal catalyst system. Ruthenium and osmium carbene compounds have been identified as effective catalysts for olefin metathesis reactions such as, for example, ROMP. Such metathesis catalysts are now well known in the art.

In preferred embodiments, the present invention involves ROMP reactions where DCPD resin compositions are cast into product molds or infused into a fiber preform. For certain applications, pigments, dyes, antiozonants and/or antioxidants, among other additives, may optionally be included.

The present invention provides, in certain preferred embodiments, polyolefin compositions containing toughness and/or hardness modulators. These polymer compositions produce articles or parts that are, for example, as tough and impact resistant as the best thermoplastics, but have the ease of fabrication of thermosets. In addition, the resin system of the present invention is tolerant to additives, fillers and fibers, such as glass, carbon, fiberglass and Kevlar, among others. As such, the modulating additives are dispersed in the polyolefin resin matrix to controllably alter various physical properties of the native polyolefin.

One aspect of the present invention is a novel composition comprising a polyolefin, prepared by the metathesis of an olefin monomer using a ruthenium or osmium carbene catalyst, and one or more toughness and/or hardness modulators. These compositions possess variable hardness, toughness and/or surface "feel" properties. Preferably, the polyolefin is poly-DCPD.

Another aspect of the present invention is an article of manufacture, such as a molded part, comprising a polyolefin, prepared by the metathesis of an olefin monomer using a ruthenium or osmium carbene catalyst, and one or more toughness and/or hardness modulators.

These and other aspects of the present invention will be apparent to one skilled in the art in light of the following detailed description of the preferred embodiments.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to polyolefin compositions having variable toughness and/or hardness properties, and to articles of manufacture made therefrom. In certain embodiments, the present invention provides toughness/hardness

modulating additives, which may be added to polyolefin resins to alter various physical properties. More specifically, addition of toughness and/or hardness modulators allows controllable modulation of the surface "feel", hardness and/or toughness of a polyolefin article. In particular cases, a modulator may serve as both a toughness and as a hardness modulator. The polyolefin compositions of the present invention are useful in a wide variety of applications, particularly for use in sports, recreational and marine equipment products.

The polyolefin compositions of the present invention may be prepared by the metathesis of olefin monomers (e.g., DCPD) and related strained cyclic olefins, polymerized with a metal catalyst system. Ruthenium and osmium carbene compounds have been identified as effective catalysts for olefin metathesis reactions such as, for example, ring opening metathesis polymerization (ROMP). Such metathesis catalysts are known in the art and have been previously described in, for example, United States Patent Nos. 5,312,940; 5,342,909; 5,728,917; 5,710,298; and 5,831,108; PCT Publications WO 97/20865 and WO 97/29135; and in United States Provisional Patent Application No. 60/115,358, filed January 8, 1999 by inventors Steven P. Nolan and Jinkun Huang entitled "Novel Metathesis Catalyst Compositions and Methods for Their Use," all of which are incorporated herein by reference.

The catalyst:olefin monomer ratio in the present invention is preferably between about 1:100 and about 1:100000. More preferably, the catalyst:monomer ratio is between about 1:1000 and about 1:10000 and, most preferably, is between about 1:3000 and about 1:8000. Particularly preferred metal catalysts include, but are not limited to, bis(tricyclohexylphosphine) benzylidene ruthenium dichloride, bis(tricyclohexylphosphine) dimethylvinylmethylidene ruthenium dichloride and bis(tricyclopentylphosphine) dimethylvinylmethylidene ruthenium dichloride.

Preferred hardness modulators include, for example, rubber-like or elastomeric additives such as polybutadienes, polyisoprenes, and the like. Polybutadienes and polyisoprenes of various sources, and of various number-average molecular weights (M_n) or weight-average molecular weights (M_w), may be utilized in the present invention as hardness modulators. Unexpectedly, the poly-DCPD resins of the present invention allow compositions containing polybutadiene to be clear or transparent, rather than opaque or translucent. This is a result of the fact that

polybutadiene becomes incorporated into the polymer backbone during the metathesis reaction, leading to little or no phase separation of the polybutadiene particles. The hardness modulators of the present invention, when added to a polyolefin resin composition, alter the hardness and/or surface "feel" of the composition compared to the unmodified or native polyolefin. In addition to butadiene- and isoprene-based elastomers, other hardness modulators include plasticizers such as dioctyl phthalate and various molecular weight hydrocarbon, fluorocarbon or similar jellies, greases and waxes; carboxylic acids and salts thereof; and co-monomers such as norbornene, cyclooctadiene, cyclooctene, cyclohexenylnorbornene, norbornadiene, di(methylcyclopentadiene), cyclopentene and/or methylcyclopentene.

The amount of hardness modulator included in the polyolefin compositions of the present invention is preferably about 0.1%-60% by weight of the olefin monomer to which it is added. More preferably, the amount of hardness modulator is about 1%-20% by weight of the olefin monomer and, most preferably, is about 2%-10%. In certain cases, hardness modulators may be included in amounts outside the preferred ranges. The determination of the appropriate amount of hardness modulator in a given polyolefin composition can be readily determined by one skilled in the art based on, for example, the degree of microphase separation desired.

Preferred toughness modulators include silicones such as, for example, polysiloxane compositions of various viscosities, molecular weights and functionalities. Particularly preferred toughness modulators include poly(dimethylsiloxane) and poly(diphenylsiloxane). Polyolefin compositions comprising such toughness modulators possess significantly increased toughness properties without significant concomitant losses in heat distortion temperature (HDT). In the case of poly-DCPD compositions comprising low molecular weight poly(dimethylsiloxane), marked improvements in thermomechanical properties are observed.

The amount of toughness modulator included in the polyolefin compositions of the present invention is preferably about 0.1%-20% by weight of the olefin monomer to which it is added. More preferably, the amount of toughness modulator is about 0.5%-10% by weight of the olefin monomer and, most preferably, is about 1%-5%. For example, poly-DCPD resins containing 3 parts per hundred low

molecular weight (MW) poly(dimethylsiloxane) (Shin Etsu DMF-50) possess notched Izod impact values in excess of 4 ft.-lb./in. and HDT values above 130°C. In certain cases, toughness modulators may be included in amounts outside the preferred ranges. The determination of the appropriate amount of toughness modulator in a given polyolefin composition can be readily determined by one skilled in the art based on, for example, the degree of phase separation desired and the degree of transparency/translucency desired. It is well known in the art that phase separation contributes to the toughness of a polyolefin material. The foregoing preferred ranges have been determined to provide polyolefin articles possessing increased toughness.

For certain applications and products (e.g., weighted golf club heads), polyolefin hybrid compositions further comprising density modulators may be preferred. Hybrid modified poly-DCPD articles can combine, for example, increased density with increased toughness. In these applications, preferred density modulators include metallic density modulators where increased density polyolefin compositions are desired, and microparticulate (e.g., microsphere) density modulators where either increased or decreased density polyolefin compositions are desired.

Examples of metallic density modulators include, but are not limited to, powdered, sintered, shaved, filed, particulated or granulated metals, metal oxides, metal nitrides and/or metal carbides, and the like. Preferred metallic density modulators include, among others, tungsten, tungsten carbide, aluminum, titanium, iron, lead, silicon oxide, and aluminum oxide. The density modulator is dispersed in the polyolefin resin matrix by stirring or mixing. The density, wear resistance and/or "feel" of a metal-filled poly-DCPD composite may be varied in a controllable manner. In particular, poly-DCPD compositions containing aluminum metal powder have a soft surface "feel", while poly-DCPD compositions containing aluminum oxide have a rough surface and are extremely wear-resistant. In the case of metal-filled poly-DCPD composite resins, articles or parts made therefrom may be produced to be isotropic, where the metallic density modulator is dispersed evenly throughout the article or part, or anisotropic, where the metallic density modulator is dispersed unevenly (either through the use of layers or a density gradient).

The amount of metallic density modulator included in the polyolefin compositions of the present invention is preferably about 1-5400 parts per hundred

parts resin (phr), by weight. More preferably, the amount of metallic density modulator is about 200-2000 phr and, most preferably, is about 300-1000 phr.

In the case of microparticulate density modulators, the poly-DCPD resin compositions of the present invention have numerous advantages over traditional thermoset polymers (e.g., epoxies, vinyl esters, unsaturated polyesters, urethanes, and silicones) in the fabrication of low- to medium-density syntactic foams. Specifically, these poly-DCPD resins combine low viscosity (<20 centipoise), long gelling times (>20 minutes), high inherent toughness, and high tensile strength. The low density and viscosity of the poly-DCPD resins of the present invention permit better wetout and packing of the microspheres, resulting in improved physical properties and, simultaneously, decreased densities (preferably, about 5%-30% decrease), compared to current state-of-the-art conventional resin systems. Preferred microparticulate density modulators include, but are not limited to, glass, thermoplastic (either expandable or pre-expanded), thermoset, and/or ceramic/silicate microspheres.

The amount of microparticulate density modulator included in the polyolefin compositions of the present invention is preferably about 1-100 phr by weight. More preferably, the amount of microparticulate density modulator is about 10-60 phr and, most preferably, is about 20-50 phr.

Preferably, in the case of poly-DCPD, the compositions of the present invention possess the following properties: tensile strength of at least about 9000 psi; elongation of at least about 4.5%; tensile modulus of at least about 350,000 psi; flexural strength of at least about 14,000 psi; and flexural modulus of at least about 30,000 psi. These values are typically 25-30% greater than those of commercially available poly-DCPD materials, such as Meton® or Telene®.

The most preferred olefin monomer for use in the present invention is dicyclopentadiene (DCPD). Various DCPD suppliers and purities may be used, such as Lyondell 108 (94.6% purity), Velsicol UHP (99+% purity), B.F. Goodrich Ultrene® (97% and 99% purities), and Hitachi (99+% purity). DCPD sources of lower purities may also be used. Other suitable olefin monomers include cyclooctadiene (COD, DuPont), cyclooctene (COE, Alfa Aesar), cyclohexenylnorbornene (Shell), norbornene, di(methylcyclopentadiene) (Aldrich), and norbornadiene (Elf Atochem).

The UV and oxidative resistance of the polyolefin compositions of the present invention may be enhanced by the addition of various antioxidants. Preferably, one or more antioxidants are included in the polyolefin resin composition at a level of about 0.1-15 phr. More preferably, the antioxidant(s) are present at a level of about 1-10 phr and, most preferably, 3-8 phr. Exemplary antioxidants include, for example, 4,4'-methylenebis (2,6-di-tertiary-butylphenol) (Ethanox 702®; Albemarle Corporation), 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl) benzene (Ethanox 330®; Albemarle Corporation), octadecyl-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate (Irganox 1076®; Ciba-Geigy), as well as Irganox 1135® (Ciba-Geigy), and the Tinuvin® (Ciba-Geigy) series of UV stabilizers. Antiozonants, such as Flexzone® (Uniroyal) may also be added.

In addition, a suitable inhibitor such as, for example, triphenylphosphine (TPP), tricyclopentylphosphine, tricyclohexylphosphine, triisopropylphosphine, pyridine, or other Lewis base, may be added to the olefin monomer. In the case of TPP inhibitor, it is preferably included in an amount of about 10-200 mg: per 64 g olefin monomer. More preferably, the amount of TPP is about 30-100 mg per 64 g olefin monomer and, most preferably, is about 50-80 mg per 64 g olefin monomer. In the case of other inhibitors, such as alkylphosphines and pyridine, the amount of inhibitor is preferably about 0.1-50 mg per 64 g olefin monomer, more preferably about 1-40 mg:64 g olefin monomer, and most preferably is about 1-30 mg per 64 g olefin monomer.

Also, various pigments or dyes may be included in the polyolefin resin compositions of the present invention for applications where color is desired. Preferred pigments include Ferro® and Dayglo® products, in an amount of about 0.05-0.5 parts per hundred of polyolefin resin. A particularly preferred class of dyes are photochromic dyes.

The polyolefin resins of the present invention are amenable to the manufacture of composites and are tolerant of additives, fillers and fibers including, but not limited to, carbon, glass, fiberglass and aramid (e.g., Kevlar® and Twaron®) and other polymer fibers (e.g., Spectra®).

The polyolefin compositions, and parts or articles of manufacture prepared therefrom, may be processed in a variety of ways including, for example, Reaction

Injection Molding (RIM), Resin Transfer Molding (RTM) and vacuum-assisted variants such as SCRIMP (Seemann Composite Resin Infusion Molding Process), open casting, rotational molding, centrifugal casting, filament winding, and mechanical machining. These processing methods are well known in the art. Various molding and processing techniques are described, for example, in PCT Publication WO 97/20865, the disclosure of which is incorporated herein by reference.

In mold casting processes, the mold may be constructed of various materials including, for example, aluminum, Teflon®, Delrin®, high- and low-density polyethylenes (HDPE and LDPE, respectively), silicone, epoxy, aluminum-filled epoxy, polyurethane and aluminum-filled polyurethane, plaster, polyvinylchloride (PVC), and various alloys of stainless steel.

The mold temperature is preferably about 20-100°C, more preferably about 30-80°C, and most preferably about 40-60°C. The molded polyolefin part or article of the present invention may also be subjected to a post-cure heating step. Preferably, the post-cure involves heating to about 60-160°C for about 10 minutes - 3 hours. More preferably, the post-cure involves heating to about 80-150°C for about 30 minutes - 2 hours and, and most preferably, involves heating to about 100-140°C for between about 45 and about 90 minutes.

The polyolefin compositions of the present invention are useful in the production of sports, recreational, and marine products and equipment which may provide performance advantages over other materials already in use. Examples of such products and applications include, but are not limited to, the following: golf tees, clubs (including weighted club heads), shafts, gradient shafts (where the formulation varies along the length of the club shaft), balls, and carts; basketball backboards; tennis rackets, squash rackets, racquetball rackets, and badminton racquets; snow boards, surfboards, boogie boards, skis, backboards, sleds, toboggans, snow shoes; baseball bats, bat coatings and end-caps, balls, and helmets; football helmets; hockey helmets, sticks, pads, and pucks; roller blade shoes, wheels, pads, and helmets; bicycle parts, frames, helmets, and trispokes; marine applications (e.g., hulls, coatings, oars, propellers, rudders, keels, masts, jet skis, boat fascia, jet skis, covers, kayaks, and canoes); camping equipment (e.g., tent stakes and supports, tubs,

matches, coolers, wedges for splitting wood, axes, hatchets, handles, shovels, and picks); pool cues, pool tables, and pool balls; diving boards, pool liners, lake liners, ladders, steps, floating lounge chairs and tables, pool cleaning equipment, and lounge chairs; motorcycles, motorcycle parts, helmets, and wind screens; archery bows and arrows; guns, rifle cases, butts, bullets, shotgun pellets, decoys, ammunition and shell cases; martial arts protective padding and weapons; soccer goal posts and pads; auto racing helmets, car parts, and bodies; polo mallets, croquet mallets and balls, and cricket bats; toys, puzzles, models, games, and novelty items including model, miniature, or toy trains, airplanes, helicopters, cars, motorcycles, rockets, spacecraft, and other model or toy vehicles, powered or unpowered; dolls and action figures and accessories therefor, recreational architectural models, two- and three-dimensional puzzles, game pieces, boards, dice, poker chips, and other game accessories and components; bowling balls and pins; tether ball pole, net supports in volleyball; All Terrain Vehicles (ATV); lawn darts, quoits, and horseshoes; and knives, knife handles, and swords.

The polyolefin compositions of the present invention are useful in the production of foams of various densities which are useful in numerous applications where properties such as weight, buoyancy, acoustic impedance, anticorrosion, antifouling, and low moisture absorption are considerations. Of particular note, the polyolefin compositions of the present invention are particularly useful in the production of golf club driver heads, exhibiting the performance of titanium drivers with the sound and "feel" of wood drivers.

Other commercial applications for the present invention include, for example, ballistics and blast containment, industrial coatings, architectural coatings, and other scratch resistant coatings, adhesives, inks, paints, and gel coats. Additionally, the compositions of the present invention are useful in polymer mixtures, interpenetrating polymer networks, fabrics, composites (fiber- or particle-reinforced), blends, alloys, elastomers, ionomers, and dendrimers, among others.

The compositions of the present invention are also useful in the manufacture of wafer carriers and other semiconductor handling equipment, as well as parts for the construction of semiconductor fabrication facilities, such as walls, fascia, sinks, and

decking. Additionally, these materials are useful as low k dielectrics and components for chemical/mechanical planarization (CMP).

In the case of polyolefin compositions or parts comprising metallic density modulators (i.e., metal composites), the present invention permits the advantageous control of balance, weight and density localization. These capabilities provide for the enhancement of the performance of, for example, golf club heads and putters and composite tooling, through selective addition and location of metallic density modulators.

In the case of polyolefin compositions or parts comprising microparticulate density modulators (i.e., syntactic foam), advantages of the compositions of the present invention are evidenced in the lightweight support and flexion enhancement of sports equipment such as archery bows, bats, sticks, and shafts. Other preferred uses for the syntactic foams of the present invention include hulls and other components of boats and submersibles, core materials for skis and surf-, snow-, and skateboards, and lightweight reinforcement of safety equipment such as pads and helmets.

EXAMPLES

Example 1

A 500 mL round bottom (RB) flask was charged with 250g DCPD (Velsicol UHP), 15g Ethanox® 702 (Albemarle), and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Velsicol UHP), 280mg triphenylphosphine (TPP) inhibitor, and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 300mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin.

Within 30 minutes, the resin appeared to be gelled and within 1 hour the golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto.

Example 2

A 500 mL RB flask was charged with 250g DCPD (Velsicol UHP), 15g Ethanox® 702 (Albemarle), and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Velsicol UHP), 400mg triphenylphosphine (TPP), and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 350mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto. This formulation greatly decreased the shrinkage in the face of the club head, probably as a result, in part, of the increased amounts of TPP inhibitor and/or catalyst.

Example 3

A 500 mL RB flask was charged with 300g DCPD (Velsicol UHP), 35g Irganox® 1076 (Ciba), and a magnetic stir-bar. The mixture was stirred and heated to 30°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Velsicol UHP), 450mg triphenylphosphine (TPP), and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 400mg

bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500ml RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto. This club head exhibited a slightly softer feel than samples prepared in Examples 1 and 2, probably due, in part, to the greater amount of Irganox® 1076, which has a plasticizing effect on the formulation.

Example 4

A 1000 mL RB flask was charged with 400g DCPD (Velsicol UHP), 25g Ethanox® 702 (Albemarle), 50g polybutadiene (Aldrich, 38,369-4), and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Velsicol UHP), 750mg triphenylphosphine, and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 600mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130° for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto. This club head exhibited a softer feel than Example 3 because

of the addition of polybutadiene. Additionally, when this formulation was poured into small (<50 mL) sample containers, gelation was accompanied by phase separation. Interestingly, upon post-cure (130°C for 1 hour), the golf club head was homogenous in appearance, despite the inclusion of polybutadiene in the formulation.

Example 5

A 1000 mL RB flask was charged with 400g DCPD (Ultrene®97 from B.F. Goodrich), 25g Ethanox®702 (Albemarle), 50g polybutadiene (Aldrich, 38,369-4) and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Ultrene®97 from B.F. Goodrich), 750mg triphenylphosphine, and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 600mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto. This club head exhibited a softer feel (similar to the sample from Example 4) due to the addition of polybutadiene. Additionally, when this formulation was then poured into small (<50ml) sample containers, gelation was accompanied by phase separation. Interestingly, upon post-cure (130°C for 1 hour), the golf club head was homogenous in appearance, despite the inclusion of polybutadiene in the formulation.

Example 6

A 1000 mL RB flask was charged with 400g DCPD (Ultrene®99 from B.F. Goodrich), 25g Ethanox®702 (Albemarle), 50g polybutadiene (Aldrich, 38,369-4) and

a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Ultrene®99 from B.F. Goodrich), 750mg triphenylphosphine, and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 600mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto. This club head exhibited a softer feel (similar to the sample from Example 4) because of the addition of polybutadiene. Additionally, when this formulation was then poured into small (<50ml) sample containers, gelation was accompanied by phase separation. Interestingly, upon post-cure (130°C for 1 hour), the golf club head was homogenous in appearance, despite the inclusion of polybutadiene in the formulation.

Example 7

A 1000 mL RB flask was charged with 400g DCPD (Lyondell 108, filtered through activated alumina), 25g Ethanox®702 (Albemarle), 50g polybutadiene (Aldrich, 38,369-4) and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Lyondell 108, filtered through activated alumina), 750mg triphenylphosphine, and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 600mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a

clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto. This club head exhibited a softer feel (similar to the sample from Example 4) because of the addition of polybutadiene. Additionally, when this formulation was then poured into small (<50ml) sample containers, gelation was accompanied by phase separation. Interestingly, upon post-cure (130°C for 1 hour), the golf club head was homogenous in appearance, despite the inclusion of polybutadiene in the formulation.

Example 8

A 1000 mL RB flask was charged with 400g DCPD (Hitachi 99), 25g Ethanox®702 (Albemarle), 50g polybutadiene (Aldrich, 38,369-4) and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Hitachi high purity), 750mg triphenylphosphine, and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 600mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club

shaft was attached thereto. This club head exhibited a softer feel (similar to the sample from Example 4) because of the addition of polybutadiene. Additionally, when this formulation was then poured into small (<50ml) sample containers, gelation was accompanied by phase separation. Interestingly, upon post-cure (130°C for 1 hour), the golf club head was homogenous in appearance, despite the inclusion of polybutadiene in the formulation.

Example 9

A 1000 mL RB flask was charged with 250g DCPD (Velsicol UHP), 15g Ethanox®702 (Albemarle), and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Velsicol UHP), 280mg triphenylphosphine, and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 300mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto.

Example 10

A 1000 mL RB flask was charged with 250g DCPD (Velsicol UHP), 15g Ethanox®702 (Albemarle), 1.5g Tinuvin®213 (Ciba) and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Velsicol UHP), 280mg triphenylphosphine, and a magnetic stir-bar. The mixture was stirred and heated to

35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 300mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto.

Example 11

A 1000 mL RB flask was charged with 250g DCPD (Velsicol UHP), 15g Ethanox®702 (Albemarle), 0.3g Ferro Corp. red pigment (34-51084) and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Velsicol UHP), 280mg triphenylphosphine, and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 300mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded red golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto.

Example 12

A 1000 mL RB flask was charged with 250g DCPD (Velsicol UHP), 15g Ethanox®702 (Albemarle), 3g dodecamethylpentasiloxane (Rhone-Poulenc) and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD (Velsicol UHP), 280mg triphenylphosphine, and a magnetic stir-bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 300mg bis(tricyclohexylphosphine) benzylidene ruthenium dichloride (sieved through a 45 mesh size sieve). After approximately 5 minutes, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 3 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf club head. The mold had been heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf club head was removed from the mold. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto.

Example 13

A 500 mL RB flask was charged with 250g DCPD monomer (B.F. Goodrich Ultrene® 99), 9g Ethanox® 702 antioxidant (Albemarle Corporation), and a magnetic stir bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD monomer (B.F. Goodrich), 0.3 g triphenylphosphine (TPP) inhibitor, and a magnetic stir bar. The mixture was stirred and heated to 35°C to yield a clear colorless solution. To this latter solution was added (with stirring) 0.37g bis(tricyclohexylphosphine) benzylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve). After approximately 1 minute, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 2 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been

previously formed into the shape of a golf club head. The mold had been heated to approximately 50°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf club head was removed from the mold and allowed to cool for 12 hours. The golf club head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature before a golf club shaft was attached thereto.

Example 14

A 500 mL RB flask was charged with 235g DCPD monomer (B.F. Goodrich), 9g Ethanox® 702 (Albemarle Corp.), 15g norbornene (Aldrich), 5g dioctyl phthalate (Aldrich), and a magnetic stir bar. The mixture was stirred and heated to 45°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD monomer (B.F. Goodrich), 0.3g triphenylphosphine (TPP), and a magnetic stir bar. This latter mixture was stirred and heated to 35°C to yield a clear colorless solution. To this solution, 0.37g bis(tricyclohexylphosphine) benzylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve) was added with stirring. After approximately 1 minute, the mixture became a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 2 minutes, the mixture turned into a clear amber solution. The solution was then poured into a mold that had been previously formed into the shape of a golf ball. The mold had been heated to approximately 50°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf ball was removed from the mold and allowed to cool for 12 hours. The golf ball was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature. This formulation was slightly softer than that of Example 13, probably due, in part, to the inclusion of dioctyl phthalate.

Example 15

A 500 mL RB flask was charged with 235g DCPD monomer (B.F. Goodrich), 9g Ethanox® 702 (Albemarle Corp.), 15g polybutadiene (Aldrich; 3000 MW), and a magnetic stir bar. The mixture was stirred and heated to 35°C to yield a clear light

yellow solution. A separate 100 mL RB flask was charged with 50g DCPD monomer (B.F. Goodrich), 0.3g triphenylphosphine, and a magnetic stir bar. The latter mixture was stirred and heated to 35°C to yield a clear colorless solution. To this solution, 0.37g bis(tricyclohexylphosphine) benzylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve) was added with stirring. After approximately 1 minute, the mixture evolved a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 2 minutes, the mixture turned into a clear amber solution. The clear amber resin solution was then poured into a mold that had been previously formed into the shape of a golf ball. The mold had been heated to approximately 50 °C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf ball was removed from the mold and allowed to cool for 12 hours. The golf ball was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature. This formulation was similar in softness to that of Example 14 above, with the addition of polybutadiene instead of dioctyl phthalate.

<u>Example 16</u>

A 500 mL RB flask was charged with 220g DCPD monomer (B.F. Goodrich), 9g Ethanox® 702 (Albemarle Corp.), 30g polybutadiene (Aldrich; 5000 MW), 0.6g black pigment (Ferro) and a magnetic stir bar. The mixture was stirred and heated to 35°C to yield a black solution. A separate 100 mL RB flask was charged with 50g DCPD monomer (B.F. Goodrich), 0.3g triphenylphosphine, and a magnetic stir bar. The latter mixture was stirred and heated to 35°C to yield a clear colorless solution. To this solution, 0.37g bis(tricyclohexylphosphine) benzylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve) was added with stirring. After approximately 1 minute, the mixture had a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 2 minutes, the mixture was a dark green/black solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf ball. The mold had been heated to approximately 50°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1

hour the molded golf ball was removed from the mold and allowed to cool for 12 hours. The golf ball was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature. This formulation was similar in softness to that in Example 14, in addition to being opaque black rather than clear amber.

Example 17

A 500 mL RB flask was charged with 150g DCPD monomer (B.F. Goodrich), 9g Ethanox® 702 (Albemarle Corp.), 135g polybutadiene (Aldrich; 3000 MW), 15g 1,5-cyclooctadiene (Aldrich), 6g t-butyl peroxide (Aldrich), and a magnetic stir bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 100 mL RB flask was charged with 50g DCPD monomer (B.F. Goodrich), 0.3g triphenylphosphine (0.3 g), and a magnetic stir bar. This latter mixture was stirred and heated to 35°C to yield a clear colorless solution. To this solution, 0.6g bis(tricyclohexylphosphine) benzylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve) was added with stirring. After approximately 1 minute, the mixture had a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 2 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf ball. The mold had been heated to approximately 50°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 2 hours the molded golf ball was removed from the mold and allowed to cool for 12 hours. The golf ball was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature. This formulation was much softer than that of Example 14, probably due, in part, to the inclusion of a greater amount of polybutadiene than previous Examples and/or the inclusion of the co-monomer cyclooctadiene. However, this formulation had a slight odor.

Example 18

A 500 mL RB flask was charged with 220g DCPD monomer (B.F. Goodrich), 9g Ethanox® 702 (Albemarle Corp.), 15g polyisoprene (Aldrich; 38,000 MW), 15g cis-cyclooctene (Avocado), and a magnetic stir bar. The mixture was stirred and

heated to 35°C to yield a yellow solution. A separate 100 mL RB flask was charged with 50g DCPD monomer (B.F. Goodrich), 0.3g triphenylphosphine, and a magnetic stir bar. This latter mixture was stirred and heated to 35°C to yield a clear colorless solution. To this solution, 0.37g bis(tricyclohexylphosphine) benzylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve) was added with stirring. After approximately 1 minute, the mixture had a clear dark amber/purple color. This solution was then added to the solution in the 500 mL RB flask with continued stirring. After approximately 2 minutes, the mixture was an amber solution. The resin solution was then poured into a mold that had been previously formed into the shape of a golf ball. The mold had been heated to approximately 50°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the molded golf ball was removed from the mold and allowed to cool for 12 hours. The golf ball was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature. This formulation was similar in softness to that of Example 14, probably due to the inclusion of polyisoprene and/or the co-monomer cis-cyclooctene. This formulation was yellow in appearance.

Example 19

A 250 mL RB flask was charged with 80g DCPD monomer (B.F. Goodrich), 3g Ethanox® 702 (Albemarle Corp.), 3g poly(dimethylsiloxane) (Shin Etsu DMF-50), and a magnetic stir bar. The mixture was stirred and heated to 35°C to yield a clear light yellow solution. A separate 50 mL RB flask was charged with 20g DCPD monomer (B.F. Goodrich), 0.1g triphenylphosphine, and a magnetic stir bar. This latter mixture was stirred and heated to 35°C to yield a clear colorless solution. To this solution, 0.14g bis(tricyclopentylphosphine) dimethylvinylmethylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve) was added with stirring. After approximately 1 minute, the mixture had a clear dark amber/purple color. This solution was then added to the solution in the 250 mL RB flask with continued stirring. After approximately 2 minutes, the mixture turned into a clear amber solution. The resin solution was then poured into a mold with cavities formed into shapes appropriate for both DTUL and Izod measurements. The mold had been

heated to approximately 40°C prior to the addition of the resin. Within 30 minutes, the resin appeared to be gelled and within 1 hour the mold was removed from the oven and allowed to cool for 12 hours. The parts were then subjected to an in-mold post-cure at 130°C for a period of 1 hour and cooled to ambient temperature. After appropriate preparation and conditioning, these parts displayed a notched Izod strength of 4.24 ft.-lb./in. and a DTUL (264 psi) of 136°C. The toughness of these parts was probably due, in part, to the inclusion of poly(dimethylsiloxane) in the formulation.

Example 20

A resin was prepared and cast as in Example 19, but using 3g poly(diphenylsiloxane) (Shin Etsu F-5W-O-100) in place of the poly(dimethylsiloxane). After appropriate preparation and conditioning, these parts displayed a notched Izod strength of 3.24 ft.-lb./in and a DTUL (264 psi) of 139°C.

Example 21

Using the same general procedure set forth in Example 13 above, two batches of resin were prepared containing:

A) 67g DCPD monomer (B.F. Goodrich), 28g polybutadiene (Aldrich; 3000 MW), 2.8g cis-cyclooctene (Avocado), 1g t-butyl peroxide (Aldrich), 0.33g black pigment (Ferro), 0.1g triphenylphosphine, and 0.124g bis(tricyclohexylphosphine) benzylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve); and

B) 50g DCPD monomer (B.F. Goodrich), 1.5g Ethanox® 702 (Albemarle Corp.), 0.33g black pigment (Ferro), 300g tungsten powder (Teledyne Advanced Materials; 150 mesh), 0.05g triphenylphosphine, and 0.124g bis(tricyclohexylphosphine) benzylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve).

A mold that had been previously formed into the shape of a golf putter head was heated to approximately 50°C. The black liquid resin A was then poured into the mold, filling it to within approximately one inch of the top (face of the putter head). Within 30 minutes, resin A appeared to be gelled and within 1 hour resin B, a viscous

black liquid, was then poured into the mold on top of gelled resin A, filling the mold completely. After 1 hour, the golf putter head was demolded and allowed to cool for 12 hours. The golf putter head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature. The resulting face-weighted putter head massed 350g and displayed a surface hardness of D50 (Shore).

Example 22

Resins A and B were prepared as in Example 21 above. In this case, however, the golf putter mold was completely filled with resin A and, after gelling 1 h in the mold, the putter head was demolded and allowed to cool for 12 hours. A portion of each of the heel and toe areas of the putter was removed, and the remainder of the part reinserted into the mold, which was then preheated to approximately 50°C. Resin B was then poured into the mold, filling in the voids created by the removal of the heel and toe sections of the putter head. After 1 hour, the part was demolded and allowed to cool for 12 hours. The putter head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to ambient temperature. The resulting heel/toe perimeter-weighted putter head weighed 300g and displayed a surface hardness of D50 (Shore).

Example 23

A putter head was prepared as described in Example 22 above, but not subjected to post-cure. After demolding, approximately 1" of the non-tungsten-filled plastic was removed from the face of the putter. The putter head was reinserted into the mold and the mold was then heated to approximately 50°C. In a 100 mL RB flask a resin was prepared containing 50g DCPD monomer (B.F. Goodrich), 1.5g Ethanox® 702 (Albemarle Corp.), 10g aluminum powder (Alfa Aesar; 3 micron), 0.05g triphenylphosphine, and 0.062g bis(tricyclohexylphosphine) benzylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve). The fresh resin was then poured into the mold, thereby filling in the void created by the prior removal of the non-tungsten-filled plastic material from the putter face. Within 30 minutes, the aluminum-filled resin appeared to be gelled and within 1 hour the molded putter head was removed from the mold and allowed to cool for 12 hours. The putter head was then subjected to a post-cure at 130°C for a period of 1 hour and cooled to

ambient temperature before a shaft was attached thereto. The overall mass and weighting characteristics of the resulting putter were similar to those of the putter in Example 21, but with a significantly softer and more solid sound and feel when used to strike (putt) a golf ball.

Example 24

A 5L RB flask equipped with a magnetic stir bar and a gas inlet adapter was charged with 2250g DCPD monomer (B.F. Goodrich), 67.5g Ethanox® 702 (Albemarle Corp.), 4.5g triphenylphosphine, and 2.497g bis(tricyclopentylphosphine) dimethylvinylmethylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve). Glass microspheres (3M; K25 grade, 720g) that had been dried at 130°C for 6 hours were gradually added to the resin in the 5L RB flask with stirring, resulting in a pale yellow mixture with the viscosity of lightly whipped cream. This resin mixture was degassed *in vacuo* to remove any trapped air bubbles (~20 min.) and then poured into a rectangular mold that had been preheated to 40°C. The part was cured in the mold at 40°C for 12 hours, then post-cured in the mold for 40 min. at 130°C, then for an additional 20 min. at 150°C. After cooling to ambient temperature, the demolded panel was found to be essentially void-free and had a density of about 34 lb./ft^3. After appropriate machining and conditioning, this material displayed a DTUL (264 psi) of 130°C, Izod strengths of 0.965 ft.-lb./in (unnotched) and 0.329 ft.-lb./in (notched), a compressive strength of 10,000 psi and a compressive modulus of 250,000. These characteristics were probably due, in part, to the inclusion of glass microspheres in the formulation.

Example 25

In the same manner as Example 24 was prepared a resin comprising: 200g DCPD monomer (B.F. Goodrich), 6g Ethanox® 702 (Albemarle Corp.), 6g poly(dimethylsiloxane) (Shin Etsu DMF-50), 0.4g triphenylphosphine, and 0.22g bis(tricyclopentylphosphine) dimethylvinylmethylidene ruthenium dichloride metathesis catalyst (sieved through a 45 mesh size sieve), and 74g glass microspheres (3M; K25 grade). The syntactic foam of this Example displayed an unnotched Izod

strength of 2.4 ft.-lb./in., probably as a result, in part, of the inclusion of poly(dimethylsiloxane) in the formulation.

What is claimed is:

1. A composition comprising:

a polyolefin prepared by the metathesis of an olefin monomer using a ruthenium or osmium carbene catalyst; and

one or more toughness and/or hardness modulators.

2. The composition of claim 1 wherein the polyolefin is poly-DCPD.

3. The composition of claim 1 wherein the one or more toughness modulators comprises a silicone.

4. The composition of claim 3 wherein the silicone is a polysiloxane.

5. The composition of claim 4 wherein the polysiloxane is a poly(dimethylsiloxane) or a poly(diphenylsiloxane).

6. The composition of claim 2 wherein the one or more toughness modulators is present in an amount between about 0.1% and about 20% by weight of the olefin monomer.

7. The composition of claim 6 wherein the one or more toughness modulators is present in an amount between about 0.5% and about 10% by weight of the olefin monomer.

8. The composition of claim 7 wherein the one or more toughness modulators is present in an amount between about 1% and about 5% by weight of the olefin monomer.

9. The composition of claim 1 wherein the one or more hardness modulators comprises polybutadiene or polyisoprene.

10. The composition of claim 1 wherein the one or more hardness modulators is a plasticizer.

11. The composition of claim 11 wherein the plasticizer is dioctyl phthalate.

12. The composition of claim 1 wherein the one or more hardness modulators comprises a carboxylic acid or a salt thereof.

13. The composition of claim 1 wherein the one or more hardness modulators comprises a co-monomer selected from the group consisting of norbornene, cyclooctadiene, cyclohexenylnorbornene, norbornadiene, cyclopentene and methylcyclopentene.

14. The composition of claim 2 wherein the one or more hardness modulators is present in an amount between about 0.1% and about 60% by weight of the olefin monomer.

15. The composition of claim 14 wherein the one or more hardness modulators is present in an amount between about 1% and about 20% by weight of the olefin monomer.

16. The composition of claim 15 wherein the one or more hardness modulators is present in an amount between about 2% and about 10% by weight of the olefin monomer.

17. The composition of claim 1 further comprising one or more density modulators.

18. An article of manufacture comprising:

a polyolefin prepared by the metathesis of an olefin monomer using a ruthenium or osmium carbene catalyst; and

one or more toughness and/or hardness modulators.

19. The article of manufacture of claim 18 wherein the article is a molded part.

20. The article of manufacture of claim 19 wherein the polyolefin is poly-DCPD.

21. The article of manufacture of claim 18 further comprising one or more density modulators.

22. The article of manufacture of claim 20 wherein the molded part is a golf club head.

23. The article of manufacture of claim 20 wherein the molded part is a golf club shaft.

24. The article of manufacture of claim 20 wherein the molded part is a baseball bat.

ABSTRACT

The present invention provides novel polyolefin compositions having variable hardness and/or toughness properties. The polyolefin compositions include: a polyolefin prepared by the metathesis of an olefin monomer using a ruthenium or osmium carbene catalyst; and one or more hardness and/or toughness modulators. The polyolefin is preferably poly(dicyclopentadiene), or poly-DCPD. Also provided are articles of manufacture, such as molded parts, produced from the polyolefin compositions. The disclosed compositions are useful in marine, recreational and sports products.

FOR UTILITY/DESIGN · CIP/PCT NATIONAL/PLANT ORIGINAL/SUBSTITUTE/SUPPLEMENTAL DECLARATIONS

RULE 63 (37 C.F.R. 1.63) DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PM & S FORM

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the **INVENTION ENTITLED : POLYOLEFIN COMPOSITIONS OPTIONALLY HAVING VARIABLE TOUGHNESS AND/OR HARDNESS**

the specification of which (CHECK applicable BOX(ES))

X → ☒ is attached hereto.
BOX(ES) → ☐ was filed on ______ as U.S. Application No. ____/______
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I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56. I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority claimed, before the filing date of this application:

PRIOR FOREIGN APPLICATION(S)

Number	Country	Day/MONTH/Year Filed	Date first Laid-open or Published	Date Patented or Granted	Priority Claimed Yes	No

I hereby claim domestic priority benefit under 35 U.S.C. 119/120/365 of the indicated United States applications listed below and PCT international applications listed above or below and, if this is a continuation-in-part (CIP) application, insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed in such prior applications, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national or PCT international filing date of this application·

PRIOR U.S. PROVISIONAL, NONPROVISIONAL AND/OR PCT APPLICATION(S)

Application No. (series code/serial no.)	Day/MONTH/Year Filed	Status pending, abandoned, patented	Priority Claimed Yes	No
60/085,981	19/05/98		X	
60/118,865	05/02/99		X	

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Pillsbury Madison & Sutro LLP, Intellectual Property Group, 1100 New York Avenue, N.W., Ninth Floor, East Tower, Washington, D.C. 20005-3918, telephone number (202) 861-3000 (to whom all communications are to be directed), and the below-named persons (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to delete names/numbers below of persons no longer with their firm and to act and rely on instructions from and communicate directly with the person/assignee/attorney/firm/ organization who/which first sends/sent this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct the above Firm and/or a below attorney in writing to the contrary.

Paul N. Kokulis	16773	Peter W. Gowdey	25872	David A. Jakopin	32995	Anita M. Kirkpatrick	32617
Raymond F. Lippitt	17519	Dale S. Lazar	28872	Mark G. Paulson	30793	Michael R. Dzwonczyk	36787
G. Lloyd Knight	17698	Paul E. White, Jr.	32011	Stephen C. Glazier	31361	W. Patrick Bengtsson	32456
Carl G. Love	18781	Glenn J. Perry	28458	Paul F. McQuade	31542	Jack S. Barufka	37087
Edgar H. Martin	20534	Kendrew H. Colton	30368	Ruth N. Morduch	31044	Adam R. Hess	41835
Kevin E. Joyce	20508	G. Paul Edgell	24238	Richard H. Zaitlen	27248		
George M. Sirilla	18221	Lynn E. Eccleston	35861	Roger R. Wise	31204		
Donald J. Bird	25323	Timothy J. Klima	34852	Jay M. Finkelstein	21082		

(1) INVENTOR'S SIGNATURE: [signature] Date: 5/14/99

MICHAEL	A.	GIARDELLO
First	Middle Initial	Family Name
Residence PASADENA	CALIFORNIA	UNITED STATES
City	State/Foreign Country	Country of Citizenship
Post Office Address	497 E. DEL MAR BLVD., #207, PASADENA, CALIFORNIA	
(include Zip Code)	91106	

(2) INVENTOR'S SIGNATURE: [signature] Date: 5/14/99

JONATHAN	G.	LASCH
First	Middle Initial	Family Name
Residence PASADENA	CALIFORNIA	UNITED STATES
City	State/Foreign Country	Country of Citizenship
Post Office Address	335 S. SIERRA MADRE BLVD., #108, PASADENA, CALIFORNIA	
(include Zip Code)	91107	

(FOR ADDITIONAL INVENTORS, check box ☒ to attach PAT 116-2 same information for each re signature, name, date, citizenship, residence and address.)

DECLARATION AND POWER OF ATTORNEY
(continued)
ADDITIONAL INVENTORS

(3) INVENTOR'S SIGNATURE: Date: 5-14-99

	CHRISTOPHER	J.	CRUCE
	First	Middle Initial	Family Name
Residence	POWAY	CALIFORNIA	UNITED STATES
	City	State/Foreign Country	Country of Citizenship
Post Office Address	13100 KIRKHAM ROAD, #202, POWAY, CALIFORNIA		
(include Zip Code)	92064		

(4) INVENTOR'S SIGNATURE: J. MacLeod Date: 5/14/99

	JESSIE	G.	MACLEOD
	First	Middle Initial	Family Name
Residence	PASADENA	CALIFORNIA	UNITED STATES
	City	State/Foreign Country	Country of Citizenship
Post Office Address	2027 EUCLID, APT. D, SANTA MONICA, CALIFORNIA		
(include Zip Code)	90405		

(5) INVENTOR'S SIGNATURE: Date:

	First	Middle Initial	Family Name
Residence			
	City	State/Foreign Country	Country of Citizenship
Post Office Address			
(include Zip Code)			

(6) INVENTOR'S SIGNATURE: Date:

	First	Middle Initial	Family Name
Residence			
	City	State/Foreign Country	Country of Citizenship
Post Office Address			
(include Zip Code)			

(7) INVENTOR'S SIGNATURE: Date:

	First	Middle Initial	Family Name
Residence			
	City	State/Foreign Country	Country of Citizenship
Post Office Address			
(include Zip Code)			

(8) INVENTOR'S SIGNATURE: Date:

	First	Middle Initial	Family Name
Residence			
	City	State/Foreign Country	Country of Citizenship
Post Office Address			
(include Zip Code)			

(9) INVENTOR'S SIGNATURE: Date:

	First	Middle Initial	Family Name
Residence			
	City	State/Foreign Country	Country of Citizenship
Post Office Address			
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